Enhancement of copolymerization of itaconic acid with N-vinyl 2-pyrrolidone by radiation in the presence of cross-linking agent

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Abstract

Enhancement of copolymerization of itaconic acid (IA) with N-vinyl 2-pyrrolidone (VP) by radiation in the presence of cross-linking agent was investigated. Hydrogels with varying IA content were prepared from the ternary systems N-vinyl 2-pyrrolidone/itaconic acid/water by irradiating with gamma-rays in the presence of a chemical cross-linker, ethylene glycol dimethacrylate (EGDMA) at ambient temperature. The incorporation of EGDMA into the ternary mixtures caused an increase in the amount of IA in the gel system up to a mole fraction of 13.7%. Hydrogels showed a typical pH response such as high pH swelling and low pH deswelling. Equilibrium volume swelling ratio at pH 7 was varied from 15–40 with changing the IA content in the gel system and irradiation dose. The equation recently modified by the authors for the determination of \( M_c \) is observed to describe the swelling behaviour of P(VP/IA/EGDMA) networks containing relatively higher amount of charged units very well. In addition to the evaluation of \( M_c \) from swelling data, the measurement of polymer solvent interaction parameter and the determination of the reaction yield of cross-links of the systems were examined.

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1. Introduction

Poly-electrolytes are polymers which contain relatively ionizable groups at levels ranging from a few mole% to 100% of the repeating unit. Poly-electrolytes may be anionic, cationic or
amphophilic and may be synthetic or naturally occurring.

As early as 1950 attempts were made for the development of environmental sensitive materials in biomedical and biotechnological applications and as a result of these studies the past 25 years has shown that different type of hydrogel systems can be used as biomaterials [1,2].

Environmental sensitivity or control of swelling ability of poly-electrolyte hydrogels under a variety of external conditions make them ideal adsorbents for removal, adsorption on enrichment of some water soluble agents such as proteins, biomolecules, metallic impurities, dyes, etc. Novel applications of hydrogels in bioseparation or as intelligent artificial systems have been widely presented in the recent literature by Ottonbrite et al. [3]. The hydrogels based on poly-electrolyte structure and synthesized via irradiation of aqueous solutions of acrylamide and N-vinyl 2-pyrrolidone with small quantities of maleic or itaconic acids are regarded as systems with potential immobilization, chelating and adsorptive properties for various bioapplications. The capacity of those gels to adsorb bovine serum albumin (BSA) was investigated by using gels with varying compositions of maleic acid [4] and itaconic acid moieties [5]. An increase in the content of diprotic acids has lead to an increase of adsorption of BSA. It has also been determined that by controlling external conditions, the BSA uptake of these hydrogels were enhanced [6].

Recently Şen and Yakar [7] also investigated the delivery of a positively charged antifungal drug terbinafine hydrochloride (TER-HCl) from itaconic acid containing vinyl pyrrolidone hydrogels. TER-HCl is a topically and orally active allylamine antifungal agent which appears to act by preventing fungal ergosterol biosynthesis via specific and selective inhibition of fungal squale oxidase. They investigated the usability of the hydrogels for the controlled release of TER-HCl and the influence of IA content and pH of the medium on the release properties of VP/IA hydrogels. They observed that TER-HCl adsorption capacity of hydrogels can be increased from 6 to 82 mg TER-HCl per gram dry gel with increasing the amount of IA in the gel system. In order to evaluate biocompatibility of acrylamide/maleic acid hydrogels, they were incubated in human serum and their biocompatibility with some biochemical parameters were controlled [8,9]. Recently, biocompatibility of P(VP/IA) hydrogels have been investigated as in vivo and some biochemical parameters of mice serum and histology of their tissues have been examined by Özdemir et al. [10].

Radiation synthesis of P(VP/IA) hydrogels, the effect of external stimuli on the swelling behaviour of these hydrogels and determination of the molecular weight between cross-links were explained in details in our previous studies [11]. In this study, radiation synthesis of VP/IA/EGDMA hydrogels, characterization of their network structure and the effect of EGDMA on the copolymerization of IA with VP have been investigated.

2. Experimental

2.1. Chemicals

The two monomers used in this study, namely N-vinyl 2-pyrrolidone (VP) and itaconic acid (IA) were obtained from Aldrich. Cross-linking agent namely ethylene glychol dimethacrylate (EGDMA) was obtained from BDH.

2.2. Preparation of hydrogels

Mixtures of 2 mL VP and 60, 120, 180 and 240 mg IA and 0.25%, 0.50%, 1.0% and 2.5% EGDMA \( W_{\text{EGDMA}} / W_{\text{VP}} \) were prepared in 1 mL of distilled water. Monomer solutions thus prepared were placed in PVC straws of 4 mm diameter and irradiated to different doses in air at ambient temperature in Gamma cell 220 type \( \gamma \) irradiator at a fixed dose rate of 0.16 kGy/h.

2.3. Composition of gels

Irradiated mixtures were dried in a vacuum oven at 315 K to constant weight and subjected to Soxhlet extraction by using water as solvent. Uncross-linked polymer and/or residual monomer was removed with this extraction from the gel structure. Extracted gels were dried again in
vacuum oven at 315 K to constant weight. Percentage gelation i.e. percentage conversion of monomers into insoluble network was based on the total weight of VP, IA and EGDMA in the initial mixture. The amount of uncross-linked IA was determined by titration of extract against NaOH (0.01 mol/L) to phenolphthalein end point.

2.4. Swelling studies

Dried hydrogels (3–4 mm thickness, 4 mm diameter) were left to swell in a buffer solution of desired pH (2–8) with ionic strength of \( I = 0.1 \) mol/L different temperatures. Swollen gels removed from the swelling medium at regular intervals were dried superficially with filter paper, weighed and placed in the same bath. The measurements were continued until a constant weight was reached for each sample. This weight was used to calculate the volume fraction \( v_{2m} \) of polymer and the equilibrium volume swelling ratio \( (Q) \) of the gel. The equations used for the calculation of \( v_{2m} \) and \( Q \) value are given below:

\[
v_{2m} = \frac{V_d}{V_s} = \left[ 1 + \rho / \rho_w (w^{-1} - 1) \right]^{-1}, \tag{1}
\]

\[
Q = \frac{1}{v_{2m}} = \frac{V_s}{V_d}. \tag{2}
\]

Here, \( V_d \) is the volume of the dry polymer sample and \( V_s \) is the volume fraction of the gel sample after equilibrium swelling, \( \rho \) and \( \rho_w \) are the densities of the dry gel and water. \( w \) is the weight fraction of polymer in the swollen gel.

3. Results and discussion

3.1. Preparation of P(VP/IA/EGDMA) hydrogels

When pure N-vinyl 2-pyrrolidone (VP) monomer has been irradiated with gamma-rays, polymerization and cross-linking reactions take place simultaneously. Total dose required for the onset of gelation was determined to be 3 kGy for pure VP and the sensitizing effect of water for the gelation of VP was very well demonstrated by Güven and Şen [12]. For the preparation of mechanically stable diprotic acid containing hydrogels the ternary mixtures of N-vinyl 2-pyrrolidone/itaconic acid/water were irradiated to 25 kGy with gamma-rays firstly by Şen et al. [11]. After synthesis of hydrogels mole percentages of monomers in the copolymeric gel and percentage gelation were calculated. Experimental results indicated that the amount of IA in the hydrogel systems could not be changed much with this preparation technique and the maximum amount of IA in P(VP/IA) hydrogel systems could be 3.2% (mole percentage).

Mole percentage of IA in the P(VP/IA/EGDMA) hydrogels prepared at 25 kGy in this study were compared with the IA content in the P(VP/IA) hydrogels in our previous study. It has been observed that (Table 1) addition of EGDMA in the initial mixture enhance the copolymerization of IA with VP.

In our previous study we could not obtain homogenous and stable hydrogels when 240 mg IA containing VP aqueous solution was irradiated with gamma-rays [12]. However, in this study by addition of only 0.25% EGDMA in the 240 mg containing 2 ml VP and 1 ml water mixture we obtained very homogenous mechanically stable hydrogel and the amount of IA could be increased up to 13.7% at low irradiation doses. These results clearly indicate that EGDMA while increasing the cross-link density of the systems also enhance the amount of IA content in the hydrogel systems. For the hydrogels prepared from 0.5%, 1.0% and 2.0% EGDMA containing initial mixtures, the cross-link density was not homogenous, they were

<table>
<thead>
<tr>
<th>Gel system</th>
<th>Mole fraction of IA</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(VP/IA)-1</td>
<td>2.4</td>
</tr>
<tr>
<td>P(VP/IA)-2</td>
<td>4.7</td>
</tr>
<tr>
<td>P(VP/IA)-3</td>
<td>6.8</td>
</tr>
<tr>
<td>P(VP/IA/EGDMA)-1</td>
<td>2.4</td>
</tr>
<tr>
<td>P(VP/IA/EGDMA)-2</td>
<td>4.7</td>
</tr>
<tr>
<td>P(VP/IA/EGDMA)-3</td>
<td>6.8</td>
</tr>
<tr>
<td>P(VP/IA/EGDMA)-4</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Irradiation dose is 25 kGy.
not mechanically stable and disintegrated into small parts during swelling so only the hydrogels prepared by using 0.25% EGDMA were investigated in this study.

3.2. Composition of hydrogels

Before the characterization experiments firstly the % gelation and conversion of monomer to gel form were investigated. Percentage gelation i.e. percentage conversion of monomer (VP), cross-linking agent (EGDMA) and IA into insoluble networks, was based on the total weight of these three monomer in the initial mixture. As can be shown from Fig. 1, the percentage gelation was increased with the increasing irradiation dose and decreased with the increasing IA concentration in the initial mixture.

The results indicate that IA still acts as an effective chain transfer agent in the copolymerization of VP in presence of the cross-linking agent, EGDMA. The amount of uncross-linked IA was determined by titration of sol fraction against NaOH to phenolphthalein end point. By using the percentage IA conversion and percentage gelation data the weight percentage of IA in the gel was also calculated. Variation of weight percentage of IA in the hydrogel with irradiation dose is given in Fig. 2. Weight percentage of IA in the gel system was not significantly changed with irradiation dose for the hydrogel systems prepared from P(VP/IA/EGDMA)-1, 2, 3 initial mixtures.

3.3. Swelling properties

For the characterization of the network structure of P(VP/IA/EGDMA) hydrogels firstly pH responsive characteristics were investigated. In order to follow the pH behaviour of the hydrogels, dry samples are allowed to swell to equilibrium in phosphate buffers with various pH at fixed ionic strength (0.1 M) and temperature (25 °C). Swollen gels removed from water at certain time intervals were dried superficially with filter paper, weighed and placed in the same bath. The measurements were lasted when a constant weight was reached for each sample. This weight was used to calculate the volume fraction \( v_{2m} \) and equilibrium volume swelling ratio, \( Q \) of polymer in a given gel sample swollen to equilibrium in water.

The effect of pH on the equilibrium volume swelling ratio of P(VP/IA/EGDMA) hydrogels prepared at 25 kGy irradiation dose are given in Fig. 3. In order to compare the effect of IA in the equilibrium volume swelling ratio, the experimentally found equilibrium volume swelling ratio values of pure PVP hydrogels [13] also represented in figure.

Consistent with poly-electrolytic behaviour swelling of hydrogels was found to increase with increasing pH. In all compositions maximum
extents of swelling were reached at pH 7.0, this being due to the complete dissociation of acidic groups of itaconic acid at this pH value. The first and second dissociation constant of IA are $pK_{a1} = 3.85$, $pK_{a2} = 5.44$, respectively [14]. Since the two dissociation constants for IA are rather close, the consecutive swelling at around these pH values overlap and only single step but broadened S shape (compared to the swelling curves of monoprotic acid containing systems) are observed in all figures. These figures represent the theoretical swelling curves of hydrogels.

The theoretical swelling curves were constructed by using solvent, polymer–solvent and polymer-based parameters given in Table 2 and experimentally calculated $M_c$ and $\chi$ parameter. The construction of theoretical swelling curves are explained in details in our previous work [15]. The experimental data points and theoretical curves are in very good accordance as can be seen from these figures. Fig. 3 shows that an increase in the ionic monomer IA, increased swelling degree due to electrostatic repulsions, and the $Q$ value was increased dramatically at high pH values. However, the variation of equilibrium volume swelling ratio with IA content has a different trend at low pH values. The equilibrium volume swelling ratio values of the hydrogels were slightly decreased with increasing IA content in the gel system up to 10%. After 10% the equilibrium volume swelling ratio values were decreased sharply for all irradiation doses. This can be explained by the increase in the cross-link density of the hydrogels with an increase of IA content in the gel system. The variation of the cross-linking density of the hydrogels were explained below.
The variation of the equilibrium volume swelling ratio at completely ionized and non-ionized states, at pH 8 and 3, are given in Figs. 4 and 5, respectively. The curves in the figures indicated that increase of the irradiation dose increases the cross-link density resulting a lower equilibrium volume swelling ratio. The increase of equilibrium degree of swelling with increase of IA content in the gel system at pH 8 can be explained by the increase of the electrostatic repulsions. Due to the large volume collapse the effect of dose in the equilibrium volume swelling ratio at the non-ionized (pH 3) state is relatively lower than the completely ionized state (pH 8). The decrease of equilibrium degree of swelling of hydrogels at pH 3 with an increase of IA content in the gel system was attributed to the increase of cross-link density. Our previous studies showed that various factors such as polymer-based, solution-based and polymer–solvent combination type parameters contribute the screen of the pH versus equilibrium volume swelling ratio curves [15]. The sharp decrease of equilibrium swelling degree of P(VP/IA/EGDMA)-4 hydrogel system at pH 3 may be also due to the variation of these parameters.

In order to explain the variation of pH-equilibrium volume swelling ratio curve style, the change in equilibrium volume swelling ratio with pH has also been evaluated for the determination of average molecular weight between cross-links, $M_c$ and polymer solvent interaction parameter, $\chi$.

### 3.4. Determination of $M_c$ and $\chi$ values of hydrogels

Eq. (3) is derived for the prediction and understanding of swelling behaviour of a hydrogel containing diprotic acid units [15].

$$\chi + \frac{(1 - 2/\phi)V_1V_2^{2/3}v_2m^{5/3}}{vM_c} = \left(\frac{[2K_{a1}K_{a2} + 10^{-\phi\text{pH}}K_{a1}]}{2[(10^{-\phi\text{pH}})^2 + 10^{-\phi\text{pH}}K_{a1} + K_{a1}K_{a2}]}\right)^2 \left(\frac{V_1\chi^2}{4I\phi^2}\right) - \ln(1 - v_2m)v_2m - v_2m^{1}$$

$$(3)$$

If the swelling data of a gel is used to plot the left-hand side of Eq. (3) (A) against the coefficient of $1/M_c$ on the right-hand side (B), a linear relation must be obtained with $\chi$ and $M_c$ values as the intercept and inverse slope, respectively.

$$A = \chi + B/M_c.$$  

(4)

Some of the information about the structural properties of hydrogels necessary for the construction of these plots are collected in Table 2. The other relevant experimental parameters to be used with Eq. (4) are as follows, ionic strength, $I = 0.1$ M, molar volume of the solvent, $V_1 = 18$ cm$^3$/mol$^{-1}$ and the number of branches originating from a cross-linking side, $\phi = 4.0$.

In the preparation of hydrogels, cross-linking agent EGDMA was used and cross-linking has been achieved in the presence of EGDMA by high energy radiation. It has been determined and known that EGDMA produce four branches originating from a cross-linked site so $\phi$ value was assumed to be 4. By using the experimentally measured polymer volume fraction, $v_2m$ of the gels in their equilibrium-swollen state and the above mentioned data, Fig. 6 is constructed for the P(VP/IA/EGDMA)-1 hydrogel systems. Very similar curves were obtained for the other hydrogel systems. $M_c$ and $\chi$ values were determined via linear regression analyses of the lines in Fig. 6. The calculated values are listed in Table 3. The effect of the presence of diprotic acid and irradiation dose on the network properties and polymer–solvent (water) interaction parameter is obvious from these results. With increasing dose the average $M_c$ values were decreased for all hydrogel systems.

![Fig. 5. Effect of irradiation dose on the equilibrium degree of swelling of P(VP/IA/EGDMA) hydrogels at pH 3.](image)
except the hydrogels prepared from P(VP/IA/EGDMA)-4 mixture. These changes were more pronounced for P(VP/IA/EGDMA)-1 mixture hydrogels and at low irradiation doses for P(VP/IA/EGDMA)-2, 3 hydrogels. A slight increase has been observed in \( M_c \) values of P(VP/IA/EGDMA)-4 mixture hydrogels when the mixture was irradiated up to 16 kGy. This slight increase was attributed to the decrease of IA content of hydrogel with irradiation dose. Due to almost constant IA content a slight decrease was observed for this gel system after 16 kGy irradiation.

With increasing amount of IA in the hydrogel structure the polymer solvent interaction parameter, \( \chi \) was also decreased. The \( \chi \) parameter of cross-linked pure PVP has been found to be 0.49 by Güven and co-workers [11]. The \( \chi \) values of P(VP/IA/EGDMA) hydrogels are given in Table 3. A value 0.45 was obtained for VP/IA/EGDMA gel with an IA content of \( \sim 3.0\% \). The decrease of \( \chi \) value with IA content may be attributed to the lower polymer–solvent interaction parameter of IA. Due to preparation difficulties of pure IA hydrogel there is not any informative data on the \( \chi \) value of pure IA in the literature.

### 3.5. Determination of the radiation yield of hydrogels cross-linking

For the determination of the reaction yield of cross-linking firstly the concentration of effective chains \( (V_e) \) must be calculated [16]. If the chain ends are ignored the concentration of effective chains is equal to \( 1/M_c \) [kmol/kg] but when the chain ends are considered a correction must be applied for chain segments, which have one end on the end of polymer molecule and are therefore ineffective in swelling. The number of such segments equals twice the original number of molecules, so a more correct expression is

\[
V_e = \frac{1}{M_c} - \frac{2}{M_n(0)}.
\] (5)

In fact the equation is only valid for the situation when the sol fraction is small or negligible. In other cases \( M_n(0) \) for sol and gel fractions are different and the cross-link density is higher in the gel than in the sol. For the situation described here this approximation is valid. \( G(X) \), cross-links, value is related to \( M_c \) and dose \( D \):

\[
G(X) = \frac{4.8 \times 10^6}{M_c D},
\] (6)

when no end-effects need be considered. When they must be included Eq. (5) turns into:

### Table 3

\( M_c \) and \( \chi \) values of P(VP/IA/EGDMA) hydrogels

<table>
<thead>
<tr>
<th>Irradiation dose (kGy)</th>
<th>P(VP/IA/EGDMA)-1</th>
<th>P(VP/IA/EGDMA)-2</th>
<th>P(VP/IA/EGDMA)-3</th>
<th>P(VP/IA/EGDMA)-4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( M_c )</td>
<td>( \chi )</td>
<td>( M_c )</td>
<td>( \chi )</td>
</tr>
<tr>
<td>8.0</td>
<td>17950 ± 890</td>
<td>0.45 ± 0.01</td>
<td>9420 ± 340</td>
<td>0.37 ± 0.01</td>
</tr>
<tr>
<td>16.0</td>
<td>14900 ± 760</td>
<td>0.45 ± 0.01</td>
<td>6550 ± 270</td>
<td>0.36 ± 0.01</td>
</tr>
<tr>
<td>16.0</td>
<td>13800 ± 440</td>
<td>0.46 ± 0.01</td>
<td>6250 ± 150</td>
<td>0.36 ± 0.01</td>
</tr>
<tr>
<td>20.0</td>
<td>13450 ± 560</td>
<td>0.46 ± 0.01</td>
<td>6100 ± 140</td>
<td>0.39 ± 0.01</td>
</tr>
<tr>
<td>25.0</td>
<td>9980 ± 310</td>
<td>0.45 ± 0.01</td>
<td>5260 ± 110</td>
<td>0.37 ± 0.01</td>
</tr>
<tr>
<td>32.0</td>
<td>7880 ± 440</td>
<td>0.44 ± 0.01</td>
<td>5020 ± 65</td>
<td>0.36 ± 0.01</td>
</tr>
</tbody>
</table>

Fig. 6. Determination of \( \chi \) and \( M_c \) values of the hydrogels prepared from P(VP/IA/EGDMA)-1 mixture.
Thus if $V_e$ is plotted against dose $D$, a straight line should be obtained. The slope gives $G(X)$ and the intercept is $2/M_n(0)$ if this is needed. However, care must be taken for such extrapolation, since for low doses, near the gelation dose, the sol fraction cannot be ignored; the repartition of cross-links, molecular chain ends as between sol and gel varies with dose, and these affect the swelling.

Eq. (7) may also be applied to the gels obtained by monomer irradiation, since in calculating the value of $G(X)$, only the slope of the straight line is involved [17]. It is, however, necessary to ensure that a complete transformation of monomer to polymer has occurred, and that the sol fraction is small or negligible. Eq. (7) may also be written in the form

$$V_e - V_{e(p)} = \frac{G(X)D}{4.8 \times 10^6} - \frac{G(X)D_{pol}}{4.8 \times 10^6}$$

or

$$V_e = \frac{G(X)D}{4.8 \times 10^6} + A.$$  \hspace{1cm} (9)

Eqs. (8) and (9) are valid for doses much higher than that needed for monomer polymerization $D_{pol}$, and the graphical image of Eq. (9) is a straight line intersecting the axis of ordinates at the point $A (A \neq 0)$.

Recently, radiation yields of the poly(vinyl pyrrolidone) cross-linking calculated on the basis of equation given above by Rosiak et al. [18]. They investigated the effect of irradiation conditions on the $G(X)$ values of VP and PVP. It was found that the numerical value of $G(X)$ much depend on the irradiation conditions. However, the $G(X)$ value (3.1) of 10% aqueous solution of PVP was very close to $G(X)$ value (3.4) of 10% aqueous solution of VP.

For the investigation of IA content on the reaction yield of cross-linking of gels Eq. (9) was used. As explained before this equation is valid for a complete transformation of monomer to polymer, and that the sol fraction is small or negligible. Due to the high sol fraction of our hydrogel systems, the values estimated according to Eq. (9) are not absolutely correct. However, the data may still be used to determine the effect of the IA content on the cross-linking efficiency. The variation of effective chains ($V_e = 1/M_e$) with irradiation dose is given in Fig. 7. The $G(X)$ value was determined via linear regression analysis of the lines in Fig. 7. The calculated values are listed in Table 4. As can be seen from the Table increase of IA content in the initial mixture relatively increased the $G(X)$ values. However due to a decrease of IA content for P(VP/IA/EGDMA)-4 mixture hydrogels up to 16 kGy and diminishing the number of cross-links decreasethe relative increase of $G(X)$ value. The $G(X)$ value of this mixture was calculated by using the $V_e$ values obtained for irradiation doses greater that 16 kGy.

As known, two consecutive junctions in network structure may be chemical cross-link, physical entanglements, crystalline regions or even polymer complexes [19,20]. Increase of $V_e$ and $G(X)$ value with increase of IA content in the gel

\begin{table}[h]
\centering
\caption{The reaction yield of cross-linking of P(VP/IA/EGDMA) hydrogels}
\begin{tabular}{|c|c|}
\hline
Gel system & $G(X)$ \\
\hline
P(VP/IA/EGDMA)-1 & 13.8 ± 1.8 \\
P(VP/IA/EGDMA)-2 & 16.7 ± 3.3 \\
P(VP/IA/RGDMA)-3 & 38.0 ± 5.7 \\
P(VP/IA/RGDMA)-4 & 17.3 ± 9.9 \\
\hline
\end{tabular}
\end{table}

![Graph](https://via.placeholder.com/150)
system indicate that IA acts as cross-linking agent. The decrease of percentage gelation and increase of cross-link density with IA content can be explained by the chain transfer agent properties of IA and formation of intramolecular cross-links and/or chain entanglements during the cross-linking of the system. The identification of possible cross-link mechanism by analyzing the network structure of these hydrogels and determination of the number of cycles and loops are still in progress in our group. We plan to publish these results as a separate article.

4. Conclusion

In this study, P(VP/IA) hydrogels were prepared by mixing the aqueous solutions of N-vinyl-2-pyrrolidone, itaconic acid and ethylene glycol dimethacrylate. Mixtures were irradiated with gamma-rays up to 32 kGy. It has been observed that addition of EGDMA in the initial mixture enhance the copolymerization of IA with VP. Hydrogels showed typical pH response such as high pH swelling and low pH deswelling. Equilibrium volume swelling ratio at pH 7 was varied from 15 to 40 with changing IA content in the gel system and irradiation dose. The increase of equilibrium degree of swelling with increase of IA in the gel system at pH 8 and the decrease at pH 3 were attributed to the increase of electrostatic repulsions in the gel system and increase of cross-link density of hydrogels, respectively.

The recently modified equation by the authors for the determination of $M_c$ has been used for the determination of the average molecular weight between consequent cross-links ($M_c$) of diprotic acid containing copolymeric hydrogels, and $\chi$ parameters. It has been observed that this equation describes the swelling behaviour of P(VP/IA/EGDMA) networks containing relatively higher amount of charged units very well.

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